

Strontium and Neodymium Isotope Stratigraphy of the Middle
Ordovician and Implications for Appalachian Weathering

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By

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Table of Contents

Abstract.....	i
Introduction.....	1
Goals and Objectives.....	2
Geologic Background and Previous Work	
Sr and Nd isotope systematics.....	3
Middle Ordovician changes in Sr and Nd.....	6
Conodont apatite versus carbonate rock as a medium for isotope studies.....	7
Methods	
Carbonate rocks.....	7
Conodont apatite.....	9
Data reporting protocols and procedures.....	10
Results.....	13
Discussion	
Preservation of primary seawater values.....	17
Significance for silicate weathering and climate.....	18
Conclusions.....	19
Recommendations for Future Work.....	20
Acknowledgements.....	21
References.....	22

Abstract

Regional tectonic events may alter the lithology and age of material weathered from the continents, leaving an imprint on the $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ compositions of seawater. Because of the long residence time of Sr compared to Nd, seawater $^{87}\text{Sr}/^{86}\text{Sr}$ changes should be globally synchronous and slow whereas $^{143}\text{Nd}/^{144}\text{Nd}$ changes may be rapid and regional. In the Ordovician, major stratigraphic shifts in both Sr (~ 0.001) and Nd (~ 10 epsilon units) have been documented. In the case of Sr, the global shift has been broadly attributed to changes in plate tectonics. For Nd, the shift has specifically been attributed to the uplift of the Appalachian Mountains (Taconic orogeny). However, no studies have been conducted that specifically address whether these changes in Sr and Nd are linked. Because the oceanic inventory of Nd is not balanced by seafloor hydrothermal input, the shift could be due to changes in continental weathering or ocean circulation patterns. A large seawater Nd shift that is due to enhanced continental weathering of young crustal rocks in the uplifted Appalachian Mountains may also be predicted to increase the flux of nonradiogenic Sr into the oceans. We have begun to test this hypothesis by producing the first integrated stratigraphic records of changes in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$. Our initial high-resolution curves were generated using bulk carbonate dissolved in acid and analyzed on a thermal ionization mass spectrometer, although we have also begun analyses with conodont apatite. These results from outcrops at Rocky Gap, Virginia and Roaring Spring and Union Furnace, Pennsylvania indicate a broad correlation of the initiation of Sr and Nd shifts in the upper Darriwilian to lower Sandbian stages (Middle-Late Ordovician transition). Other sections further west (e.g., Nevada) will be analyzed to compare the timing of Sr and Nd shifts in different epeiric sea water masses.

Introduction

In the Middle Ordovician, a significant drop in the $^{87}\text{Sr}/^{86}\text{Sr}$ of seawater has been documented (Veizer et al., 1999; Shields et al., 2003; Young et al., 2009). This drop is evidence of a change in silicate weathering, most likely related to a change in the composition of the source rocks being weathered on land in some region of the Ordovician Earth. Due to the globally homogenous nature of the $^{87}\text{Sr}/^{86}\text{Sr}$ seawater signal however, the source of this change has not yet been confidently determined. During this time period, extensive volcanism and uplift was occurring on the eastern margin of North America as part of the Taconic Orogeny (present-day Appalachian Mountains). Young et al. (2009) suggest that the changes in silicate weathering caused by these events in the Taconic region are responsible for the global $^{87}\text{Sr}/^{86}\text{Sr}$ decrease seen, a hypothesis this study will examine in detail.

Goals and Objectives

The main goal of this study is to establish whether changes in the weathering of silicate rocks as a result of the Taconic Orogeny could be related to the shifts in both the $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ seawater trends seen in the Taconic Region during the Middle Ordovician (Darriwilian Stage; ~467 to 458 million years ago; see Figure 1). As part of this goal, this study will attempt to establish if a correlation in the timing and overall trend of the Sr and Nd shifts occur in multiple field sections in the Taconic region. We hypothesize that if the change in weathering due to the Taconic uplift is contributing to the global decline in $^{87}\text{Sr}/^{86}\text{Sr}$, the $^{143}\text{Nd}/^{144}\text{Nd}$ data from the region will rise due to the fact that uplifted young volcanic rocks will have formed with relatively low amounts of radiogenic Sr (low $^{87}\text{Sr}/^{86}\text{Sr}$) but high amounts of radiogenic Nd (high $^{143}\text{Nd}/^{144}\text{Nd}$). We further hypothesize that if Taconic weathering changes are responsible for the Sr shift, then the Nd and Sr shifts should initiate simultaneously. This study

will also attempt to determine if conodont apatite is a suitable medium for isotopic analyses in comparison to analyses using bulk micrite (limestone). We hypothesize that the conodont apatite will provide similar values to those obtained using limestone and will preserve the same trend. We further hypothesize that conodont apatite may provide less altered values than the micrite analyses.

	Global			North American		N. Am. Graptolite	N. Atlantic Conodont	N. Am. Midcontinent Conodont	Time Slice	Stage Slice
	System	Series	Stage	Series	Stage					
Millions of Years	Ordovician	Upper Ordovician	Sandbian	Mohawkian	Turinian	bicornis	tenuis	alobatus	5b	Sa2
							aculeata			
							quadrid.			
							compressa			
							undatus			
		Middle Ordovician	Darnvilian	Whiterockian	Not distinguished	gracilis	sweeti	variabilis	5a	Sa1
		Middle Ordovician	Dapingian	Rangerian	Rangerian	austro-dentatus	sinuosa	norrand-icus	4a	Dw1

Figure 1: Chronostratigraphic chart of the Middle and Upper Ordovician, including Global and North American Series and Stage names, North American Midcontinent and North Atlantic Conodont Zones, North American Graptolite Zones, Time Slices (Webby et al., 2004) and Stage Slices (Bergstrom et al., 2008). The yellow bar highlights the interval of interest, where the Sr shift initiates.

Geologic Background and Previous Work

Sr and Nd isotope systematics

It is widely recognized that the seawater ratio of isotopes of certain elements may vary through time or geographically based on the behavior of the isotopes or environmental factors that influence them. Strontium and neodymium are two such elements that have gained wide acceptance as proxy indicators useful in paleoenvironmental reconstructions. Both Sr and Nd have a radiogenic isotope, ^{87}Sr and ^{143}Nd , that is the daughter product of a radioactive decay process. Both also have stable isotopes, ^{86}Sr and ^{144}Nd , against which the radiogenic daughter products can be compared. These isotopic ratios preserved in rocks are a function of the rock's age and composition. ^{87}Sr is the decay product of ^{87}Rb . Rubidium is an element that, because of its size and valence, tends to be preferentially incorporated into the liquid phase during fractional crystallization of a magma, while Sr tends to be concentrated into plagioclase. Because of this, as fractional crystallization progresses the Rb/Sr ratio of the residual magma gradually increases (Faure 1986). As a result, granitic rocks (which are the result of residual magmas in which higher melting temperature minerals have already crystallized and been removed from the melt) are enriched in Rb compared to Sr, while basaltic rocks are depleted in Rb (Faure 1986). This enrichment in Rb compared to Sr leads to a higher ratio of $^{87}\text{Sr}/^{86}\text{Sr}$ in granitic rocks than basaltic rocks. Neodymium behaves in an opposite manner to strontium. ^{143}Nd is the decay product of ^{147}Sm . As fractional crystallization of a magma progresses Nd is concentrated in the liquid phase relative to Sm. As a result, as differentiation of a magma progresses the Sm/Nd ratio decreases. Because of this, granitic rocks have a lower $^{143}\text{Nd}/^{144}\text{Nd}$ ratio than basaltic (Faure 1986).

The isotopic ratio of the rocks also depends on the age of the rock. All silicate rocks, as well as the mantle reservoir, are becoming more radiogenic with time as ^{87}Rb and ^{147}Sm undergo decay into their daughter products. The rate of this change differs in the mantle and different

crustal rock packages however, due to the different initial ratios of Rb/Sr and Sm/Nd. Until a package of magma separates from the mantle, it continues to become more radiogenic at the same rate as the mantle, as they share the same Rb/Sr and Sm/Nd ratios. Once the magma has separated from the mantle however, it begins to become more radiogenic at a different rate. In the Rb/Sr system, once the magma separates from the mantle, it begins to become more radiogenic at a faster rate than the mantle, due to the enrichment of Rb in the melt. Because of this, older rocks are more radiogenic than younger rocks (even when the rocks are of similar composition) because the older rock has been changing at the faster rate for a longer period of time (see Figure 2). Likewise, in the Sm/Nd system, once a package of magma has separated from the mantle it begins to become more radiogenic at a slower rate than the mantle, due to the depletion of Sm in the melt. Therefore older rocks are less radiogenic than younger rocks (see Figure 2) (Allegre, 2008).

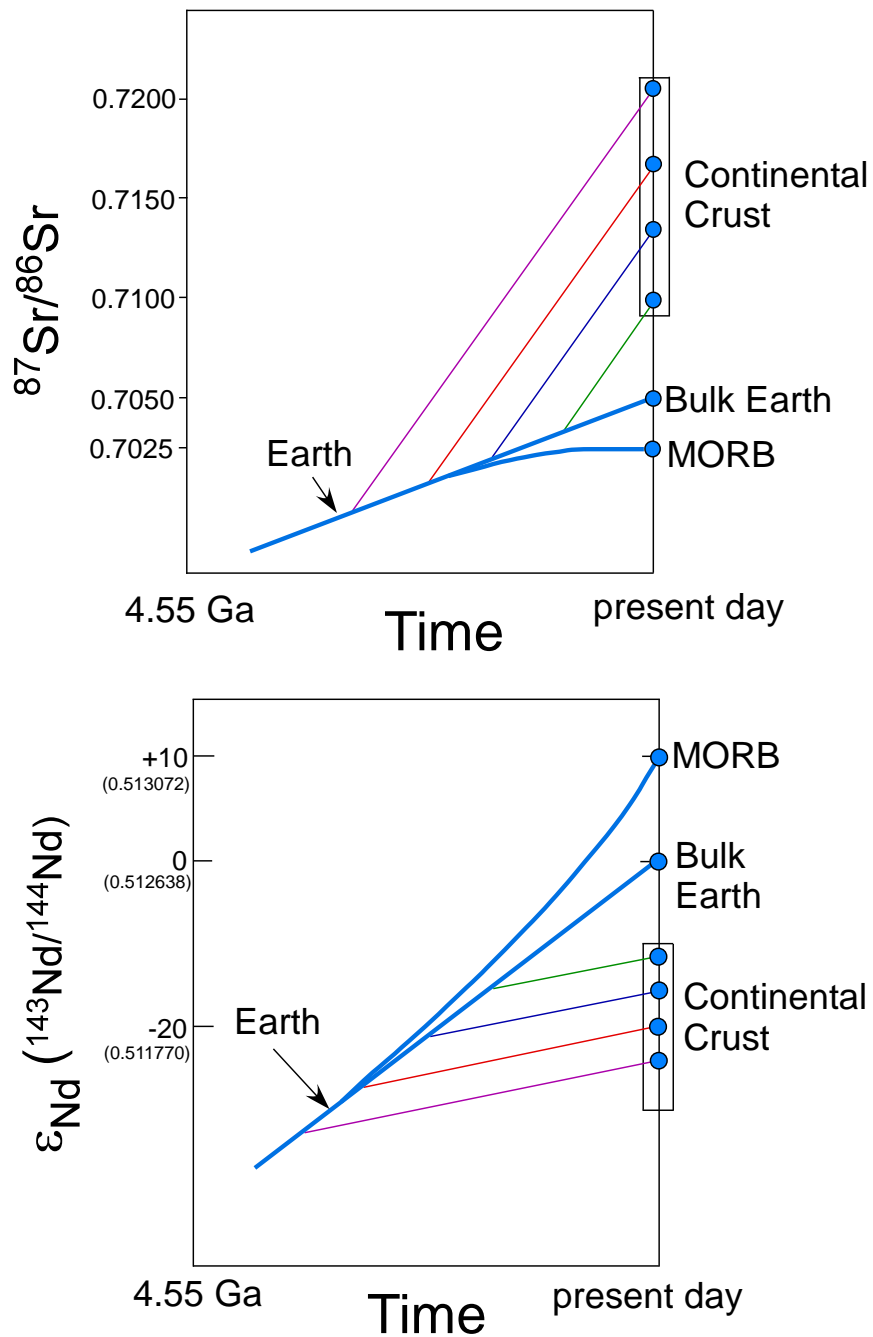


Figure 2: Diagrams showing the evolution of Sr and Nd over time and their inverse relationships.

The multicolored lines show the isotopic evolution of magma that has separated from the mantle at different times (purple for oldest crust, green for youngest etc.). Values in parentheses are $^{143}\text{Nd}/^{144}\text{Nd}$ values. Both isotopic ratios become more radiogenic towards the top of the graph.

Modified after Allegre (2008).

Because of these relationships, the seawater values of $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ can act as a proxy for the composition or age of rocks being weathered. While both Sr and Nd can provide indications of weathering changes, they operate on different spatial and temporal scales. Strontium has a residence time of approximately 5×10^6 years, which is longer than the mixing time of the oceans, approximately 10^3 years (Faure 1986). As a result, seawater $^{87}\text{Sr}/^{86}\text{Sr}$ averages the global riverine input and is homogenous throughout the global oceans and relatively slow to respond to changes in particular source areas. Neodymium, however, has a residence time on the order of 10^2 years, so it does not stay in the ocean long enough to become homogeneously mixed (Faure 1986). Because of this, seawater Nd ratios vary from region to region and can offer insight on changes in weathering on a smaller, more local scale with the potential to capture abrupt shifts in the nature of the source rock being weathered.

Middle Ordovician changes in Sr and Nd

The Middle Ordovician drop in $^{87}\text{Sr}/^{86}\text{Sr}$ has been broadly attributed to changes in tectonic forces, but no specific cause has yet been agreed upon. During the Middle Ordovician, a significant rise in $^{143}\text{Nd}/^{144}\text{Nd}$ has also been documented in studies aimed at understanding the provenance of clastic sedimentary rocks as a test of tectonic models of mountain building. This Nd rise has been attributed to increased weathering of juvenile sources, possibly juvenile Grenville crust uplifted as a result of the Taconic Orogeny, or island-arc basalts off the Laurentian coast (Andersen and Samson, 1995; Gleason et al., 2002; Wright et al., 2002). In addition, a marine transgression occurred during this time period, which may have flooded low-lying ancient rock sources (cratonic rocks in the Transcontinental Arch; Fanton et al., 2002)(see

Figure 3). The flooding of this old source rock would have removed it from weathering and contributed to the rise in the seawater $^{143}\text{Nd}/^{144}\text{Nd}$.

Conodont apatite versus carbonate rock as a medium for isotope studies

This study also seeks to determine if conodont apatite is a suitable medium for isotope analyses. Conodonts are small eel-like organisms that lived from the Late Cambrian through the Late Triassic. They produced small phosphatic tooth-like elements as part of their feeding apparatuses. These elements are preserved in many marine rocks from the Cambrian to the Triassic. These elements were biomineralized in equilibrium with seawater, so they should preserve the isotopic ratios of seawater at the time the organism was alive.

Previous studies using conodonts for the purpose of determining the Sr isotopic ratios of seawater have yielded conflicting conclusions on whether conodonts actually preserve the isotopic ratios of seawater at the time of death of the organism (Holmden et al., 1996; Needham, 2007). In some studies where co-existing elements and limestones were analyzed, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios from the conodonts were typically found to be more radiogenic than those yielded from the limestones (Holmden et al., 1996). In others, however, the conodonts were actually found to be less radiogenic and preserve a better record of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the time (Needham, 2007). More work is required to definitively determine the usefulness of conodont apatite in Sr isotope analyses.

Methods

Carbonate rocks

The samples for micritic limestone analyses in this study were collected at three field sites; Rocky Gap, Virginia, and Union Furnace and Roaring Spring, Pennsylvania (see Figure 3).

The Pennsylvania sections did not preserve the entire stratigraphic sequence in question in either locality, and were combined to create a composite section. The Union Furnace rocks overlay the Roaring Spring rocks, and both were collected with a slight overlap in the Loysburg/Hatter formations to ensure no gaps were present in the sequence. The rock samples were cut to remove weathered material, and sonicated in deionized water to remove loose sediment. Powder was generated using homogenous micrite lacking bioclasts and veins. For Sr samples, ~60 mg of powder was pre-treated in buffered 1M ammonium acetate (pH 8) and digested for 30 minutes in 4% acetic acid (8% acetic used on dolomites) (Montanez, 1996). The supernate was collected and spiked with a ^{84}Sr tracer. For Nd samples, 2 grams of powder was dissolved with 6N HCl and passed through a 0.2 μm Teflon PTFE filter to remove any remaining particles before adding 100 mg of $\text{Fe}(\text{Cl})_2$ (Fantoni et al., 2002). Concentrated ammonium hydroxide was added dropwise until a precipitate formed. This precipitate was then dissolved in 2N HCl and spiked using a mixed ^{147}Sm - ^{150}Nd solution. The resulting liquid for both Sr and Nd samples was put through cation exchange resin using 2N HCl to separate the Sr and rare earth fractions. The rare earth fraction was then dissolved in 0.15N HCl and the Nd and Sm fractions were separated using hydrogen di-2-ethylhexyl phosphate coated PTFE Teflon powder using HCl elution. Sr and Nd samples were diluted using 0.3N HCl. Samples were loaded on Re filaments using a Ta_2O_5 activator for Sr and H_3PO_4 for Nd. They were run on a Finnigan/MAT 261 fully automated, variable collector mass spectrometer using dynamic collection mode for Sr and Nd and static collection mode for Sm at the Radiogenic Isotope Laboratory at the Ohio State University (separation and spectrometry procedures of Foland and Allen, 1991).

Conodont apatite

The conodont elements used in this study were taken from insoluble residues left from Dr. Jeff Bauer's PhD thesis work (Bauer, 1987). These samples were collected by Dr. Bauer from the McLish Formation in the I-35 section of the Arbuckle Mountains of Oklahoma (see Figure 3), from the same time period as the Virginia and Pennsylvania sections. Conodont elements are separated from the surrounding rock using buffered formic acid and concentrated using magnetic and heavy liquid separation. Dr. Bauer performed the above collections and separations for these samples. For this study, individual elements were picked from the residues, brushed with water to remove any visible sediment, then sonicated and rinsed in deionized water to remove any further contaminating particles. Whole elements, as well as any well-preserved fragments (not badly digested by acid from the separation procedures) were used, with a preference for large elements lacking a basal cavity. Approximately 0.3-0.5 mg of elements were used for each analysis. The elements were leached in 0.2 N ammonium acetate for fifteen minutes (Needham, 2007) then dissolved in 1 mL of 6 N HCl. The resulting liquid then underwent the methods described above for separation of Sr using cation exchange resin and mass spectrometer analysis.

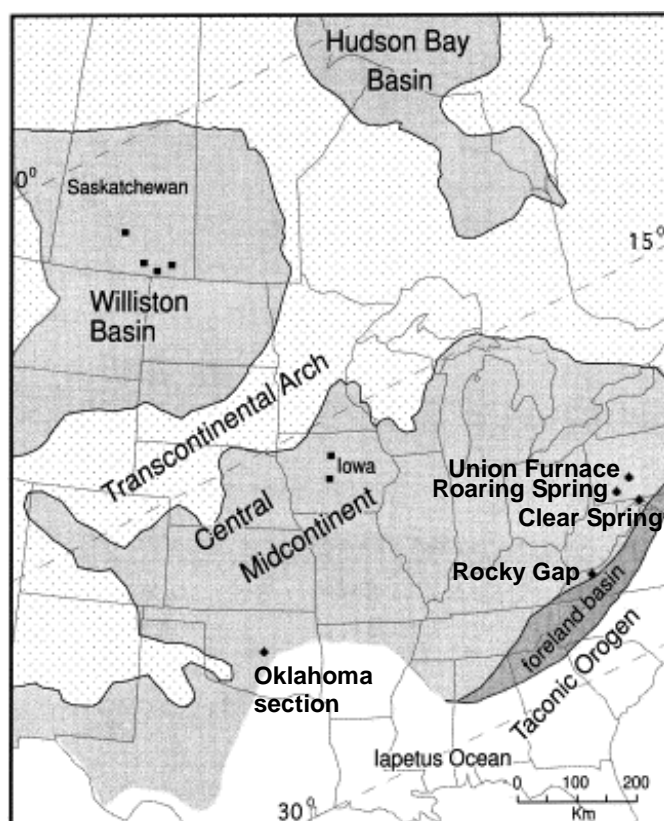


Figure 3: Paleomap of North America during the beginning of the Late Ordovician. Field locations for this study are marked with diamonds (Union Furnace, Roaring Spring, Clear Spring, Rocky Gap and the Oklahoma section). Squares represent sample locations for Fanton et al. (2002), from which this figure was modified. Gray areas represent epeiric seas.

Data reporting protocols and procedures

$^{143}\text{Nd}/^{144}\text{Nd}$ is expressed here in units of $\epsilon_{\text{Nd}}(\text{T})$, which accounts for ^{147}Sm decay into ^{143}Nd over time and back calculates to the ϵ_{Nd} value at the time of deposition. The $\epsilon_{\text{Nd}}(\text{T})$ curves were generated using a third order polynomial line of best fit (calculated for Rocky Gap, approximated for Union Furnace/Roaring Spring). The $^{87}\text{Sr}/^{86}\text{Sr}$ seawater curves were drawn through the least radiogenic values at each horizon, as these samples are thought to be the least

altered. More radiogenic values tend to correspond to samples with lower concentrations of Sr (see Figure 4). As diagenesis has a tendency to lower the concentration of Sr in the rocks being altered, more radiogenic samples with low Sr concentrations are considered to be less trustworthy. Additionally, in Figures 4, 5 and 6 the open circles represent dolomitized rocks, which are possibly altered (see Discussion).

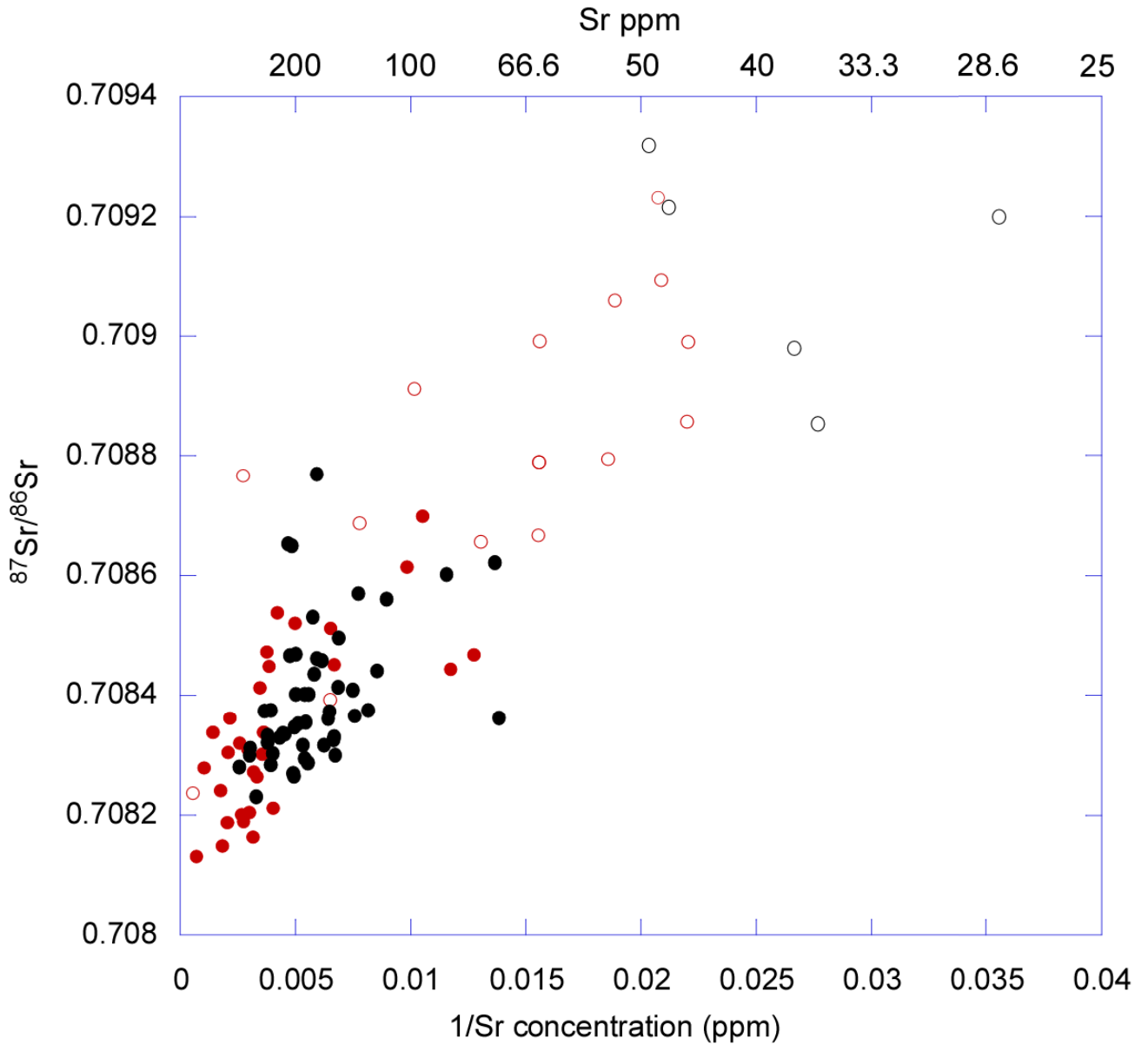


Figure 4: Graph of $^{87}\text{Sr}/^{86}\text{Sr}$ ratio vs. $1/\text{concentration}$. Black data points correspond to data from Rocky Gap, Virginia, and red data points correspond to data from the Union Furnace/Roaring Spring, Pennsylvania composite. The graph shows that higher Sr concentrations correspond to less radiogenic values, which are considered unaltered or less altered. The open circles are the dolomites from the Knox and Bellefonte formations, some of which appear to be significantly altered.

Results

Figures 5 and 6 show the results of the micrite analyses at Rocky Gap and the Pennsylvania composite section for both Sr and Nd. Both the Rocky Gap section and the Pennsylvania composite show a significant decrease in $^{87}\text{Sr}/^{86}\text{Sr}$ starting in the upper Darriwilian and continuing into the early Sandbian, following the global trend outlined in Veizer et al. (1999), Shields et al. (2003), and Young et al. (2009).

At Rocky Gap, $^{87}\text{Sr}/^{86}\text{Sr}$ decreases from 0.7087 to 0.7082 during this time, excluding the radiogenic, altered samples in the Knox dolomite. At Union Furnace/Roaring Spring, the $^{87}\text{Sr}/^{86}\text{Sr}$ curve begins a rapid decrease at 0.7087 that levels out at 0.7081 during this time interval. Global seawater values reported in Veizer et al. (1999), Shields et al. (2003), and Young et al. (2009) show a decrease from 0.7086 to 0.7078 during this same time period. Both sections also show an increase in $\epsilon_{\text{Nd}}(\text{T})$ from the Darriwilian to Sandbian. At Rocky Gap the $\epsilon_{\text{Nd}}(\text{T})$ values increase from -17 to -7 during the interval of the $^{87}\text{Sr}/^{86}\text{Sr}$ decrease. At Union Furnace/Roaring Spring the $\epsilon_{\text{Nd}}(\text{T})$ values show a general increase from approximately -16 to -8, albeit with significant scatter during the interval of the $^{87}\text{Sr}/^{86}\text{Sr}$ decrease compared to Rocky Gap (see Discussion).

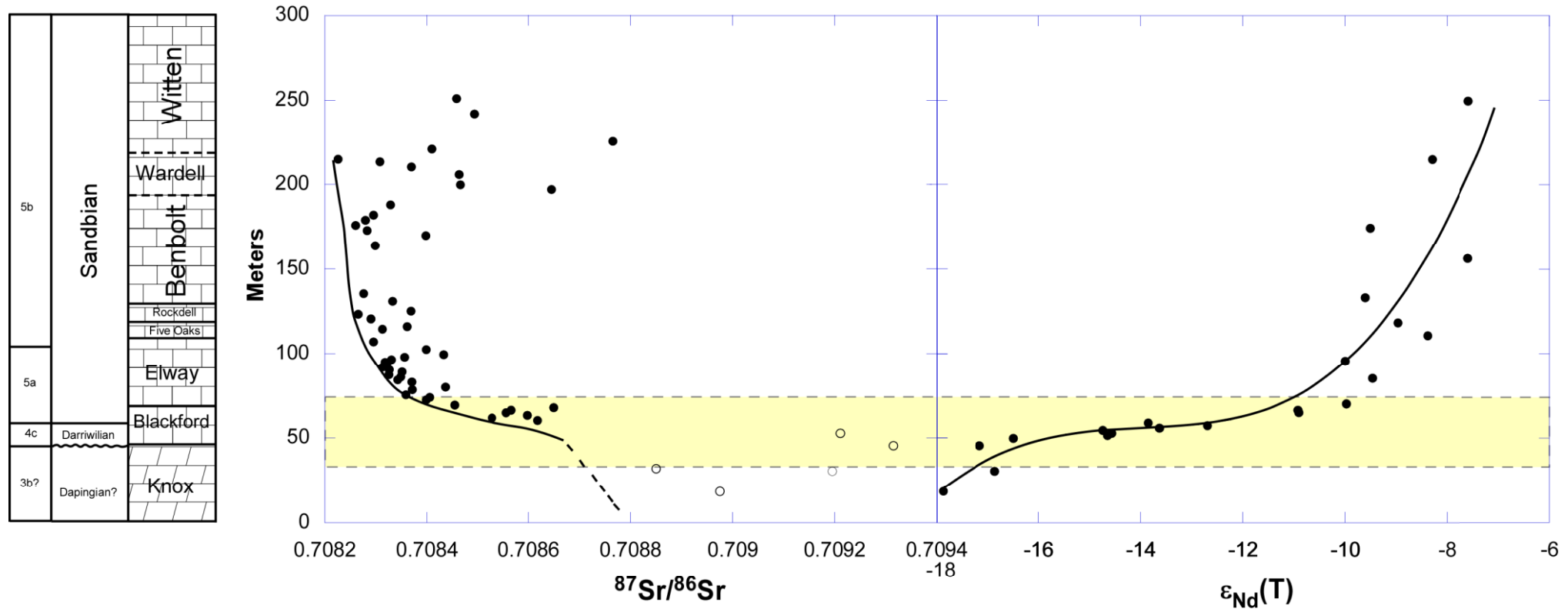


Figure 5: $^{87}\text{Sr}/^{86}\text{Sr}$ and $\epsilon_{\text{Nd}}(\text{T})$ curves for Rocky Gap, Virginia with local formations, global stages, and time slices from Webby et al. (2004). The dashed line in the $^{87}\text{Sr}/^{86}\text{Sr}$ curve represents the global seawater trend that the curve should be following; the open circles represent dolomite samples from the Knox Formation, some of which are thought to be altered (see Figure 4). The yellow box highlights the interval where the rapid shift in Sr is occurring, and corresponds with the yellow box in Figure 1.

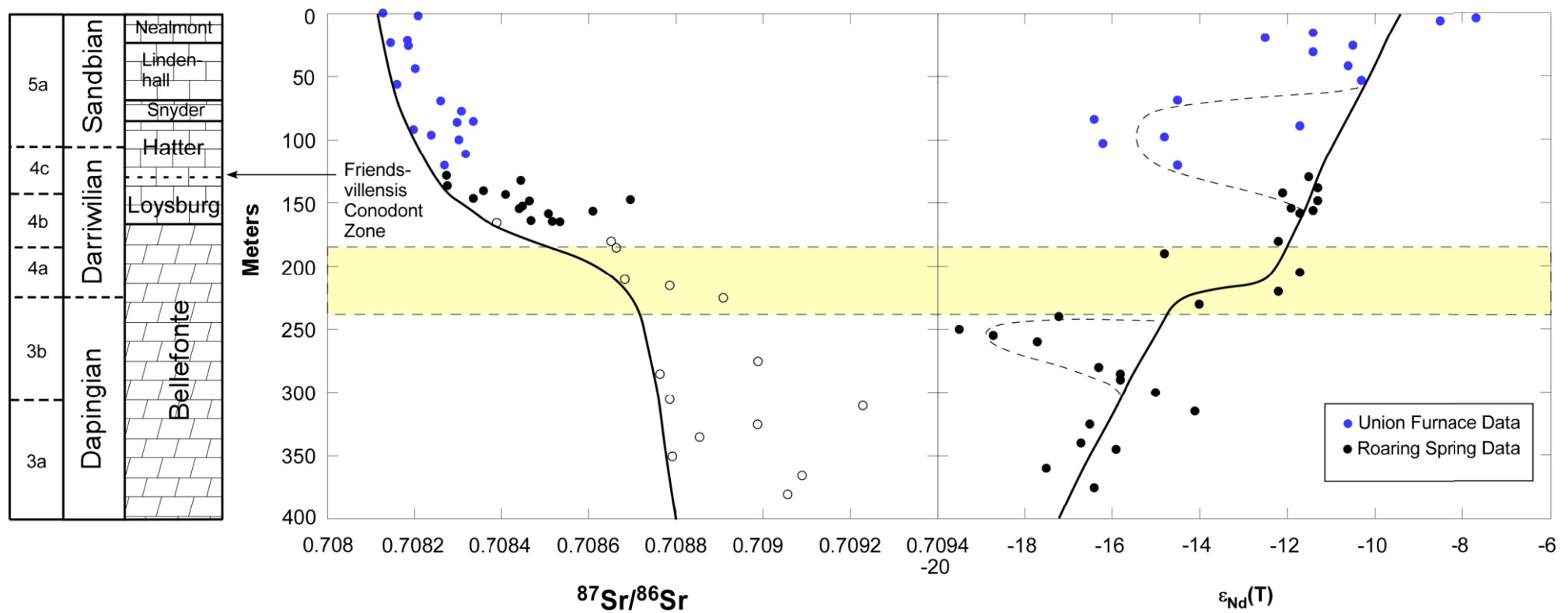


Figure 6: $^{87}\text{Sr}/^{86}\text{Sr}$ and $\epsilon_{\text{Nd}}(\text{T})$ curves for Union Furnace/Roaring Spring Pennsylvania with local formations, global stages, and time slices from Webby et al. (2004). The graph is a composite of two separate locations, with data from Union Furnace in blue and data from Roaring Spring in black. The open circles represent dolomite samples from the Bellefonte Formation, some of which are thought to be altered (see Figure 4). The dashed lines in the $\epsilon_{\text{Nd}}(\text{T})$ curve represent short-term, local excursions (see Discussion). The yellow box highlights the interval where the rapid shift in Sr is occurring, and corresponds with the yellow box in Figure 1. Biostratigraphy for the Pennsylvania section was done by Dr. Stig Bergstrom of the Ohio State University.

Figure 7 shows the conodont data from three samples in the McLish Formation in Oklahoma plotted alongside the corresponding $^{87}\text{Sr}/^{86}\text{Sr}$ values from micrite analyses (when applicable). For two of the samples, limestones and conodont elements from the same stratigraphic height were analyzed. The youngest conodont sample has no corresponding micrite analysis however. Previously performed micrite analyses for several samples in the Oklahoma section have shown that this section also preserves the global $^{87}\text{Sr}/^{86}\text{Sr}$ decrease through the Middle Ordovician, with values becoming less radiogenic stratigraphically upward. The conodont samples also preserve this trend, becoming less radiogenic as they move up section. Though there are only three data points, these samples tentatively support the hypothesis that conodont elements preserve at least seawater trends, if not actual seawater values.

In both cases where both a conodont value and a micrite value from the same stratigraphic height exist, the value yielded by the conodont elements is less radiogenic than the value yielded by the micrite by approximately 0.0001. This may offer further support for Needham's conclusion that conodont elements tend to be less altered than micrite and preserve more original, less altered seawater values (see Discussion).

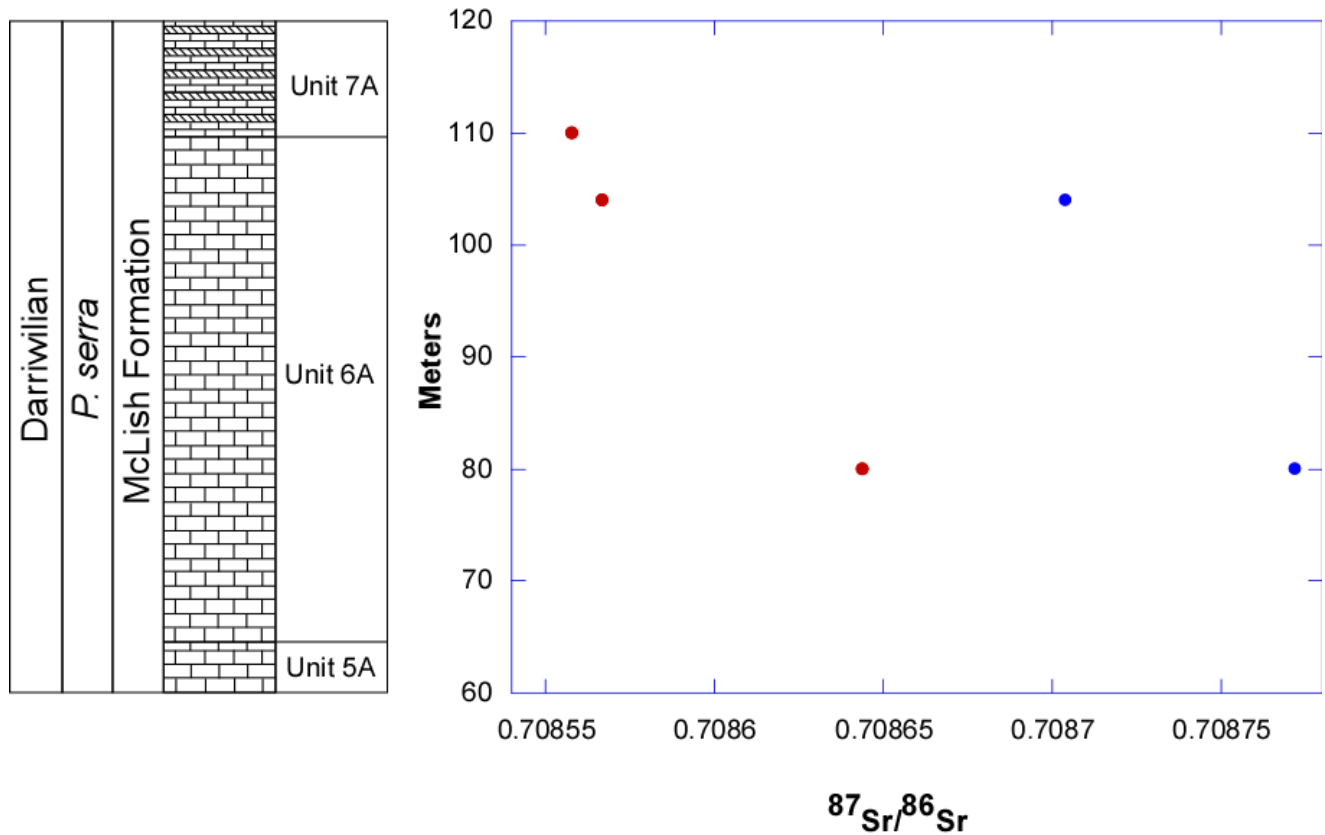


Figure 7: $^{87}\text{Sr}/^{86}\text{Sr}$ values for the McLish Formation with local formations and units, global stages, and North American Mid-Continent Conodont Zones. Red values are from analyses performed on conodont apatite; blue values are from analyses performed on micrite.

Discussion

Preservation of primary seawater values

The $^{87}\text{Sr}/^{86}\text{Sr}$ values reported at both Rocky Gap and Roaring Spring are at some horizons more radiogenic than those reported in previous Ordovician studies using brachiopod calcite (e.g., Veizer et al., 1999; Shields et al., 2003) or micrite (Young et al., 2009). There are several possible causes of this difference. Dolomites are the dominate rock type in the lower parts of both the Virginia and Pennsylvania sections and likely are more prone to alteration of primary seawater values due to the very low initial Sr concentrations. In the Pennsylvania composite

section the least radiogenic of the dolomite samples, however, likely still preserve the original seawater values and contain relatively high Sr concentrations compared to Rocky Gap. In Rocky Gap the dolomitized samples were not included in the $^{87}\text{Sr}/^{86}\text{Sr}$ seawater curve, as they no longer appear to preserve original values. In addition to dolomites, rocks with high clay content (insoluble residue), such as the upper part of the Rocky Gap section, are generally prone to alteration due to leaching of Sr from noncarbonate sources. Additionally, uncertainty in both sections in biostratigraphic correlation could lead to slight differences compared to the seawater curves of Veizer et al. (1999) and Young et al. (2009). Despite the radiogenic values at some horizons, the trend of the data still follows the expected seawater trend, excluding the altered section of Rocky Gap that was not included in the $^{87}\text{Sr}/^{86}\text{Sr}$ curve drawn for the section.

The $\epsilon_{\text{Nd}}(\text{T})$ data at Union Furnace/Roaring Spring is noisy, but thought to be unaltered. Diagenesis likely does not alter the $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of limestones or dolomites, as the concentration of Nd in seawater is much lower than the concentration of Nd in the rock, removing the ability of the pore fluids to alter the Nd ratios (Faure 1986). The noise is likely due to the short residence time of Nd (on the order of 10^2 years), which preserved small scale, local changes in weathering sources and their riverine distributions. Despite the scatter, the overall trend of the data still shows an increase in $\epsilon_{\text{Nd}}(\text{T})$ values corresponding to the decrease in $^{87}\text{Sr}/^{86}\text{Sr}$ as seen at Rocky Gap.

Significance for silicate weathering and climate

In both sections the $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ show a general temporal correlation, with Nd increasing during the interval that Sr is decreasing, supporting a change in weathering in the Taconic region as a partial cause of both the local Nd shift and the global Sr shift. This correlation is consistent with changes in silicate weathering on land as a cause of the global Sr isotope shift, as opposed to higher rates of seafloor spreading that lead to higher levels of

hydrothermal alteration with fresh basalt, a process that has been proposed by previous authors to cause drops in $^{87}\text{Sr}/^{86}\text{Sr}$ such as the drop observed in the Middle Ordovician (Veizer et al., 1999). The $^{143}\text{Nd}/^{144}\text{Nd}$ in the Taconic region would not be affected by such an increase in seafloor spreading rates, so the presence of the Nd shift is evidence for changes in silicate weathering on land. Due to the alteration of the Sr values in the dolomites in the older parts of both sections however, definite conclusions on the timing of the onset of the Sr isotope drop relative to the Nd rise can not be made. Further work is needed to determine if the onset of both shifts correlate (see Recommendations for Future Work).

The likely scenario proposed here involves weathering young volcanic rocks such as basalt with low $^{87}\text{Sr}/^{86}\text{Sr}$ and high $^{143}\text{Nd}/^{144}\text{Nd}$ during the Darrwilian Stage of the Ordovician. This should have affected the global rate of removal of carbon dioxide from Earth's atmosphere. Basaltic rock is enriched in calcium-bearing minerals (compared to rocks of more felsic composition). When these rocks are chemically weathered they release Ca^{+2} ions that react with bicarbonate ions in seawater to produce calcium carbonate rock. This reaction consumes carbon dioxide, storing it in carbonate rocks and removing it from interaction with the atmosphere. The climate during the Darrwilian Stage of the Ordovician is poorly known, but may represent a time during which the oceans cooled to become similar to the modern day oceans for the first time in the Phanerozoic period (Trotter et al., 2008).

Conclusions

The correlation seen in the two Appalachian sections (Rocky Gap, Virginia and Pennsylvania composite) between decreasing Sr values and increasing Nd values in the same time interval offers good evidence that the cause of the global Sr shift was due to changes in weathering in the Taconic region. Possible sources that could provide the high $^{143}\text{Nd}/^{144}\text{Nd}$ and

low $^{87}\text{Sr}/^{86}\text{Sr}$ material are the juvenile Grenville crust uplifted in the Taconic Orogeny and island arc basalts off the Laurentian coast (Anderson and Samson, 1995)

The conodont data, while sparse, tentatively supports the conclusion that conodont elements can preserve the general trend of $^{87}\text{Sr}/^{86}\text{Sr}$ seawater values, and that they preserve less radiogenic, less altered values that are closer to the actual seawater values than those yielded by micrite.

Recommendations for Future Work

Attempts to determine the age of the rocks at Rocky Gap and Union Furnace/Roaring Spring using Sr chemostratigraphy were not entirely successful due to the altered nature of the dolomitized older parts of the sections. Further work is needed to better correlate with other sections, particularly the Nevada section from Young et al. (2009), which is better constrained biostratigraphically. Further work to correlate the Appalachian sections and the Nevada section using carbon isotope chemostratigraphy or conodont biostratigraphy should help to better constrain the age of the Nd shift.

Due to the altered dolomite sections, further work is also required to determine the initiation points for the Sr and Nd shifts to determine if they are indeed synchronous. Continued work in a well-dated, thick Middle Ordovician section in Maryland (Clear Spring, MD) from the same time period may yield more conclusive results.

To further determine if changes in source material from the Taconic region are responsible for the Sr seawater change, Nd analyses of the Nevada and Oklahoma sections could also be done. Neodymium is a regional signal, and Nevada was not in circulation with the seawater in the Appalachian region during the Middle Ordovician. Because of this, if the cause of the Sr decrease is in the Taconic region, the Nd curve from Nevada should not show the same

correlation to the Sr curve that is seen in the Appalachian sections (or should show the shift later, once circulation was reestablished during sea level rise). The Oklahoma section might show a similar neodymium curve as the Appalachian sections, though with a slight offset in the initiation of the shifts, as Oklahoma is further removed from the Taconic region.

The conodont data, while promising, is somewhat scarce with only three data points. Processing of more samples from the Oklahoma section to determine if they also follow the trends seen in this study would offer more concrete evidence that the perceived trends are real, and that conodonts do in fact accurately preserve $^{87}\text{Sr}/^{86}\text{Sr}$ seawater trends.

Acknowledgements

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